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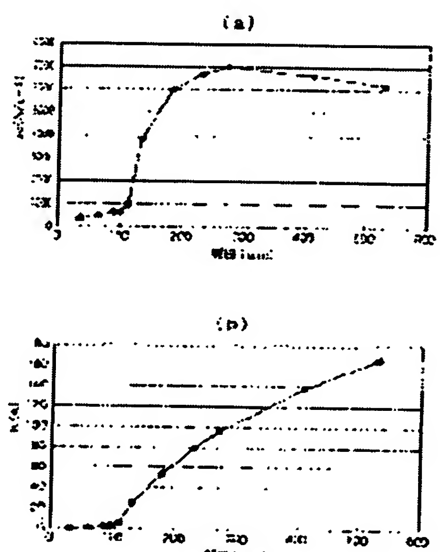
(54) THICK FILM OF OXIDE SUPERCONDUCTOR AND METHOD FOR MANUFACTURE THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a thick film of an oxide superconductor which is formed on the surface of a substrate or a base body and has high Jc and Ic.

SOLUTION: The thick film of the oxide superconductor having high Jc and Ic and a film thickness of ≥130 μm is prepared by weighing and mixing prescribed amounts of raw materials containing respective elements Bi, Pb, Sr, Ca, and Cu, and adding an organic binder and organic vehicle to the raw materials after steps of calcining, pulverizing, and drying to prepare a (Bi, Pb) 2+aSr2Ca2Cu3Oz superconductive paste, applying the paste to the surface of the substrate or the base body to a thickness of ≥260 μm, and after drying it first subjecting the coating to firing for 100 hours at 835 to 840° C, , then to pressurizing and further to firing for 100 hours at 835 to 840° C.



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CLAIMS

[Claim(s)]
[Claim 1]
It is the thick film of the oxides superconductors containing Bi, Pb, Sr, calcium, and Cu which are formed in the front face of a substrate or a base,
The oxides-superconductors thick film characterized by the thickness of said thick film being 130 micrometers or more.
[Claim 2]
It is the thick film of the oxides superconductors containing Bi, Pb, Sr, calcium, and Cu which apply oxide superconductivity composition powder to the front face of a substrate or a base, calcinate this, and are formed,
The oxides-superconductors thick film with which more than 30wt% of Pb contained into the oxide superconductivity composition powder applied in the first half is characterized by being held in said thick film.
[Claim 3]
It is the thick film of the oxides superconductors containing Bi, Pb, Sr, calcium, and Cu which are formed in the front face of a substrate or a base,
The oxide superconductivity composition powder which has the mole ratio of Bi:Pb:Sr:calcium:Cu=1.85:0.35:1.90:2.05:3.05 850 degrees C, After calcinating for 100 hours, 3t /is compressed by the pressure of 2 cm using CIP. The bulk object of the oxide superconductivity object which calcinates for 100 hours and contains 850 more degree C (however, 0< a<0.5) of 2(Bi, Pb) +aSr2calcium2Cu3Oz(es) is prepared. By EPMA When the signal strength of Pb contained in the bulk object core is measured and the signal strength is standardized with 1,
The oxides-superconductors thick film characterized by the relative intensity of the signal of Pb at the time of measuring the signal strength of Pb contained in said thick film of the surface right above of said substrate or a base by EPMA being 0.67 or more.
[Claim 4]
The oxide superconductivity structure characterized by forming the oxides-superconductors thick film of a publication in the front face of a substrate or a base at either of claims 1-3.
[Claim 5]
It is the manufacture approach of the thick film of the oxides superconductors containing Bi, Pb, Sr, calcium, and Cu which are formed in the front face of a substrate or a base,
The manufacture approach of the oxides-superconductors thick film characterized by applying an oxides-superconductors paste to the front face of said substrate or a base so that it may become thickness 260 micrometers or more, and calcinating with the burning temperature of 830-850 degrees C in case said thick film is produced.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]
This invention relates to the thick film and its manufacture approach of the oxides superconductors containing Bi, Pb, Sr, calcium, and Cu which have high critical current density.
[0002]
[Description of the Prior Art]
Various application products are devised by forming oxides superconductors in oxide substrates, such as MgO, an alumina, and YSZ, or an oxide base, and a list in the shape of film, and operating them as a metal substrate or metal bases, such as Ag, Au, Pt, and nickel.
After adding the organic binder suitable as an approach of forming these oxides superconductors in the shape of film for the oxide superconductivity composition powder which is oxide superconductivity object powder and making it the shape of a paste, using screen printing, a doctor blade method, a spray method, etc., it applies to the front face of said substrate or a base, it calcinates, and the technique in which the thick film of the oxides superconductors of the polycrystalline substance is made to form is tried.
[0003]
It is thought that the technique in which the thick film of these oxides superconductors is made to form is very cheap and more advantageous than not needing the large-scale and expensive equipment which needs the high vacuum system represented by an expensive single crystal substrate, PVD, CVD, etc. in respect of a manufacturing cost, and is the technique nearest to utilization.
Conventionally, as an oxides-superconductors ingredient in which this thick film is made to form, the YBCO system which has the presentation of Y1Ba2Cu3Ox, Bi2212 system which has the presentation of Bi2Sr2calcium1Cu2Oy, and Bi2223 system which has the presentation of 2(Bi, Pb) +aSr2calcium2Cu3Oz (however, 0< a<0.5 is the same the general following.) have mainly been tried.
When applying the thick film of oxides superconductors to a practical product here, as for critical current density (it is hereafter indicated as Jc.), two or more 3,500 A/cm** is called for in liquid nitrogen temperature.
From this viewpoint, the Prior art of the oxides superconductors mentioned above is explained briefly.
[0004]
For example, in liquid nitrogen temperature, as for the oxides-superconductors thick film (it is hereafter indicated as a thick film.) containing Y1Ba2Cu3Ox, hundreds A/cm2 is obtained as Jc. About the critical current value (it is hereafter indicated as Ic.), about several A are obtained by the thick-film sample with a width of face [of 5mm], and a thickness of 100 micrometers.
However, since crystal orientation cannot gather easily when the thick film of oxides superconductors, i.e., the gestalt of the polycrystalline substance, is taken, Y1Ba2Cu3Ox is difficult to obtain Jc more than the above.
[0005]

Moreover, for example, the thick film containing Bi2Sr2calcium1Cu2Oy is a promising ingredient -- in liquid nitrogen temperature, 6000 A/cm2 is obtained as Jc, and about ten to 15 A is obtained about Ic by the thick-film sample with a width of face [of 5mm], and a thickness of 50 micrometers.
However, if this ingredient thickens sample thickness in order to obtain higher Ic, a superconduction property will fall rapidly. Consequently, the more it thickens thickness, even if the value of Jc equalized as the whole thick film falls, for example, produces a thick film with a width of face [of 5mm], and a thickness of 100 micrometers, Ic is about 20A and, the more will fall up to about 4000 A/cm2 by Jc. And even if it thickens more than this and thickness, Ic will not become large in proportion to it, but a fall of Jc equalized conversely will be enhanced.
[0006]
Moreover, a thick-film sample with a thickness of 100 micrometers is manufactured the place to current, in liquid nitrogen temperature, about several A are obtained by hundreds A/cm2 as Jc, and, as for the thick film containing 2(Bi, Pb)+aSr2calcium2Cu3Oz, they are acquired by the sample with a width of face of 5mm as Ic, for example. However, Jc which this thick film shows is about [of the value expected from the value of Jc which the bulk object containing same (Bi, Pb) 2+aSr2calcium2Cu3Oz has] 1/10. Furthermore, if thickness of a thick film is made thick to 100 micrometers or more in order to obtain higher Ic, since oxides superconductors will separate from the front face of a substrate or a base in the case of said baking, difficult ** of the oxides superconductors containing 2(Bi, Pb) +aSr2calcium2Cu3Oz is carried out as a charge of thick-film material.
[0007]
[Problem(s) to be Solved by the Invention]
The technical problem which this invention tends to solve from an above-mentioned situation is offering the thick film and its manufacture approach of the oxides superconductors which have high Jc and high Ic.
[0008]
[Means for Solving the Problem]
The 1st means for solving a technical problem concerning this invention is the thick film of the oxides superconductors containing Bi, Pb, Sr, calcium, and Cu which are formed in the front face of a substrate or a base,
It is the oxides-superconductors thick film characterized by the thickness of said thick film being 130 micrometers or more.
[0009]
Jc and Ic which a thick film has were able to be greatly raised by setting to 130 micrometers or more thickness of the thick film of the oxides superconductors containing Bi, Pb, Sr, calcium, and Cu which are formed in the front face of a substrate or a base.
[0010]
It is the thick film of the oxides superconductors containing Bi, Pb, Sr, calcium, and Cu which the 2nd means applies oxide superconductivity composition powder to the front face of a substrate or a base, calcinate this, and are formed,
More than 30wt% of Pb contained into the oxide superconductivity composition powder applied in the first half is the oxides-superconductors thick film characterized by being held in said thick film.
[0011]
Having the above-mentioned configuration, the thick film of the oxides superconductors containing Bi, Pb, Sr, calcium, and Cu which are formed in the front face of a substrate or a base had high Jc and high Ic.
[0012]
The 3rd means is the thick film of the oxides superconductors containing Bi, Pb, Sr, calcium, and Cu which are formed in the front face of a substrate or a base,
The oxide superconductivity composition powder which has the mole ratio of Bi:Pb:Sr:calcium:Cu=1.85:0.35:1.90:2.05:3.05 850 degrees C, After calcinating for 100 hours, 3t /is compressed by the pressure of 2 cm using CIP. The bulk object of the oxide superconductivity object

which calcinates for 100 hours and contains 850 more degree C (however, $0< a<0.5$) of 2(Bi, Pb) +aSr2calcium2Cu3Oz(es) is prepared. By EPMA When the signal strength of Pb contained in the bulk object core is measured and the signal strength is standardized with 1,
It is the oxides-superconductors thick film characterized by the relative intensity of the signal of Pb at the time of measuring the signal strength of Pb contained in said thick film of the surface right above of said substrate or a base by EPMA being 0.67 or more.
[0013]
Having the above-mentioned configuration, the thick film of the oxides superconductors containing Bi, Pb, Sr, calcium, and Cu which are formed in the front face of a substrate or a base had high Jc and high Ic.
[0014]
The 4th means is the oxide superconductivity structure characterized by forming the oxides-superconductors thick film of a publication in the front face of a substrate or a base at either of the 1st to 3rd means.
[0015]
By the above-mentioned configuration, the oxide superconductivity structure which has high Jc and high Ic was able to be obtained with the cheap manufacturing cost.
[0016]
The 5th means is the manufacture approach of the thick film of the oxides superconductors containing Bi, Pb, Sr, calcium, and Cu which are formed in the front face of a substrate or a base,
In case said thick film is produced, it is the manufacture approach of the oxides-superconductors thick film characterized by applying an oxides-superconductors paste to the front face of said substrate or a base so that it may become thickness 260 micrometers or more, and calcinating with the burning temperature of 830-850 degrees C.
[0017]
By taking the above-mentioned manufacture approach, the thick film of the oxides superconductors containing Bi, Pb, Sr, calcium, and Cu which have the thickness beyond 130mmicro can be manufactured.
[0018]
[Embodiment of the Invention]
In order to obtain the thick film of the oxides superconductors which have high Jc and Ic, after this invention person prepared the oxide superconductivity composition powder containing Bi, Pb, Sr, calcium, and Cu, added the organic binder and the solvent and made it the shape of a paste, he applied to the front face of a substrate or a base, and considered relation between the burning temperature of the applied paste, and peeling by the front face of a substrate or a base. Consequently, when calcinated at the temperature exceeding 850 degrees C currently performed conventionally, since the rate of crystal growth of 2(Bi, Pb)+aSr2calcium2Cu3Oz was large, it solved that growth in the substrate and the direction of a substrate front face of a thick film advanced rapidly, consequently peeling by the front face of a substrate or a base was caused.
[0019]
Then, the result of having repeated trial-and-error in order that this invention person might control above-mentioned peeling, (Bi, Pb) A 2+aSr2calcium2Cu3Oz thick film 830-850 degrees C by [which is temperature lower than the conventional burning temperature] calcinating in 835-840 degrees C more preferably Even if it formed the thick film 130 micrometers or more on the front face of a substrate or a base, it found out that Jc and Ic of about [that peeling does not occur] and a thick film increased greatly.
[0020]
Hereafter, the thick film which calcinated the paste (it is hereafter indicated as a superconduction paste.) of the oxide superconductivity composition powder containing Bi, Pb, Sr, calcium, and Cu which were applied to the front face of a substrate or a base, and was obtained is explained as an example as an example of the thick film of the oxides superconductors containing Bi, Pb, Sr, calcium, and Cu.

[0021]
Weighing capacity is carried out and the various powder of Bi 2O3, and PbO, SrCO3, CaCO3 and CuO is mixed so that it may become a desired mole ratio. At this time, CaO or calcium (OH)2 is sufficient as CaCO3. Moreover, the raw material prepared so that it might become the mole ratio of a request of each element of Bi, Pb, Sr, calcium, and Cu with a wet coprecipitation method etc. may be used.
Next, temporary quenching of this mixed powder is carried out, and temporary-quenching powder is obtained. Temporary-quenching conditions are 750 degrees C - 850 degrees C more preferably than 600 degrees C - 1000 degrees C, and are 3 hours - 50 hours.
Next, the above-mentioned temporary-quenching powder is put into a ceramic spot with organic solvents, such as a zirconia ball and toluene, and ball grinding is performed. While grinding temporary-quenching powder finely and raising homogeneity by this actuation, the thermal reactivity of temporary-quenching powder can be raised in the following baking process.
[0022]
The temporary-quenching powder of the shape of a slurry which ball grinding ended is dried with a dryer.
Next, ball grinding which mentioned above the temporary-quenching powder after desiccation after baking on 750-850 degrees C and the baking conditions of 3 - 50 hours was performed, and repeat superconduction composition powder was prepared for this "baking-ball grinding-desiccation" 1 - 5 times (preferably 2 - 3 times) after that.
The prepared superconduction composition powder was mixed with the proper organic binder and the organic vehicle, and the superconduction paste was obtained by kneading using 3 rollers etc.
[0023]
It calcinated, after making the front face of a substrate or a base apply and dry the obtained superconduction paste by various kinds of thickness, and it considered as the thick-film sample of oxides superconductors.
Since the thickness of a thick-film sample is set in general to one half of the thickness of the applied superconduction paste, for obtaining thickness (about 260 micrometers and 530 micrometers), it should just apply a superconduction paste by the thickness of about 1060 micrometers for obtaining 130-micrometer thickness, for example.
Baking conditions are 835-840 degrees C more preferably the burning temperature of 830-850 degrees C, and firing time was made into 50 - 100 hours.
To the thick-film sample after baking, 2-3t /was compressed by the pressure of 2 cm using CIP (cold isostatic press) equipment. This is for carrying out orientation so that the a-b plane to which supercurrent tends to flow the plate crystal of 2(Bi, Pb)+aSr2calcium2Cu3Oz generated by baking may be arranged in the energization direction.
835-840 degrees C and firing time calcinated again the thick-film sample after pressurization / compression more preferably the burning temperature of 830-850 degrees C in 50 - 100 hours.
[0024]
Then, even if it was the thick-film sample which has thickness 100 micrometers or more, it became possible to prepare to the thick-film sample which does not cause peeling from the front face of a substrate or a base after baking, and has about 1000 micrometers of thickness.
Consequently, 11 kinds of 2(Bi, Pb)+aSr2calcium2Cu3Oz thick-film samples which have 30-530 micrometers of thickness in the gestalt of this operation were prepared.
[0025]
Jc of the superconduction property which 11 kinds of this thick-film sample showed, and Ic are explained referring to drawing 1 , drawing 2 (a), and (b).
Drawing 1 is a table showing the measurement result of the thickness of 11 kinds of thick-film samples, and Jc and Ic. Drawing 2 (a) It is the graph by which took Jc (A/cm2) of a thick-film sample for the result of drawing 1 along the axis of ordinate, and the thickness (micrometer) after baking of a thick-film sample was taken and shown on the axis of abscissa, and drawing 2 (b) is the graph by which took Ic (A) of a thick-film sample for the result of drawing 1 along the axis of ordinate, and the thickness

(micrometer) of a thick-film sample was taken and shown on the axis of abscissa.
In addition, Jc of a thick-film sample and Ic measurement were performed by computing Jc from the cross section of Ic which used the silver paste for the thick-film sample, prepared the electrode, cooled to 77K by liquid nitrogen, measured Ic by 4 terminal method (electrization), and then was measured, and a sample.
[0026]
When the thickness of the thick film formed in the front face of a substrate or a base is 110 micrometers or less so that more clearly than drawing 1 and drawing 2 (a), although Jc of a thick-film sample is increased gradually with the increment in thickness, the value is about two 1000 A/cm in about two 400 A/cm and 110 micrometers at 30 micrometers. However, if thickness becomes thick from this, the value of Jc increases sharply, and about two 3850 A/cm will be reached in 130 micrometers, and it will reach about two 7000 A/cm in 270 micrometers.
Although the increment in Jc was not seen but the gradual decrease inclination was rather seen even if thickness became thick more than this, 6200 A/cm2 was shown also in 530 micrometers of thickness.
[0027]
On the other hand, when the thickness of a thick film is 110 micrometers or less, it increases gradually with the increment in thickness and Ic of a thick-film sample is about 5.5A about 0.6A and in 110 micrometers at 30 micrometers, so that more clearly than drawing 1 and drawing 2 (b). However, when thickness became thick from this, it increased sharply, it reached to about 25A in 130 micrometers, and it reached about 95A in 270 micrometers, and the value of Ic continued the increment with the increment in thickness further, and reached about 165A in 530 micrometers.
[0028]
Next, quantitative analysis by ICP was carried out about Pb concentration which chooses six kinds of thick-film samples, 85 micrometers of thickness, 110 micrometers, 130 micrometers, 180 micrometers, 270 micrometers, and 530 micrometers, removes and extracts the thick film from 11 kinds of prepared thick-film samples, and is contained in a thick film, and quantitative analysis by ICP was carried out also about Pb concentration of the superconduction composition powder used for coincidence as a superconduction paste.
This result is explained referring to drawing 8 .
Drawing 8 is the graph which was computed from Pb concentration of the superconduction composition powder used for the axis of ordinate as a superconduction paste, and Pb concentration contained in a thick-film sample and which took the maintenance rate of Pb from superconduction composition powder to the inside of a thick-film sample, and took the thickness value of a thick-film sample along the axis of abscissa.
[0029]
From drawing 8 , when the thickness value of a thick-film sample was 110 micrometers or less, it became clear that the maintenance percentage of Pb was less than 20%. On the other hand, when a thickness value was 130 micrometers, the maintenance rate of Pb exceeded 30% and it became clear that the maintenance rate of Pb also increased with the increment in a thickness value after that.
[0030]
Furthermore, line analysis of the direction of thickness was performed about Pb concentration contained in a thick film using EPMA to six kinds of thick-film samples, 85 micrometers of thickness, 110 micrometers, 130 micrometers, 180 micrometers, 270 micrometers, and 530 micrometers.
This result is explained referring to drawing 3 .
Drawing 3 is the graph by which took the relative intensity of the signal of Pb contained in an axis of ordinate in the direction of thickness of a thick-film sample, and the location of the direction of thickness in a thick-film sample was shown on the axis of abscissa.
Here, it asked for the relative intensity of said signal of Pb by the following approaches.
[0031]
First, weighing capacity was carried out, it mixed and each powder of Bi 2O3, and PbO, SrCO3, CaCO3 and CuO was used as mixed powder so that it might become the mole ratio of 1.85:0.35:1.90:2.05:3.05.

Under the atmospheric-air ambient atmosphere, 780 degrees C, temporary quenching of this mixed powder was carried out for 10 hours, and it was used as temporary-quenching powder.
It put into the ceramic spot with both this temporary-quenching powder, the zirconia ball as grinding media, and the toluene as a solvent, and it set to the rotation base, ball grinding was performed, and the temporary-quenching powder of the shape of a slurry which ball grinding ended was dried with the dryer.
Again, under the atmospheric-air ambient atmosphere, 780 degrees C, after calcinating the temporary-quenching powder which this desiccation completed for 10 hours, ball grinding was carried out and it was dried. In addition, grinding conditions and desiccation conditions were performed on these 1st conditions.
And the line obtained superconduction composition powder for a series of actuation of this "baking-grinding-desiccation" 3 times.
[0032]
The bulk object of an oxide superconductivity object with a diameter [of 25mm] and a thickness of 1.5mm which compresses it by the pressure of 2 cm 3t /using CIP after calcinating 850 degrees C of superconduction composition powder obtained at the above-mentioned process for 100 hours, calcinates 850 more degrees C for 100 hours, and has the presentation of 2(Bi, Pb)+aSr2calcium2Cu3Oz was prepared. An example of this bulk object showed consistency about 5.1 g/cm3, and Jcabout 5000 A/cm3.
The signal strength of Pb contained in said bulk object core is measured by EPMA, and the signal strength is standardized with 1.
On the other hand, in the thick-film sample, the location of the surface right above of a substrate or a base was set to 0 micrometer, and the location in a thick film was shown with the distance from there to a thick-film front face, and the signal strength of Pb contained in each of that location was measured by EPMA, and it computed and asked for relative intensity with the signal strength of said standardized bulk object.
In addition, in order to make in agreement the Measuring condition in EPMA measurement with said bulk object and said thick-film sample, as for both samples, measuring to coincidence is desirable.
Furthermore, in drawing 3 , a 130-micrometer sample is a thick line, the 180-micrometer sample was the Taichi point chain line, the sample of 85 micrometers of thickness is a continuous line among said thick-film samples, and the thick dashed line showed [a 110-micrometer sample is a broken line and / a 270-micrometer sample is ********** and] the 530-micrometer sample.
[0033]
In the case of the thin thick-film sample of thickness, also not only in the front face of a thick film but in the deep part nearest to the front face of a substrate or a base, it became clear that the signal strength of Pb was falling so that more clearly than the result of drawing 3 .
For example, in the case of the thick-film sample of 85 micrometers of thickness, even place [where the signal strength of Pb is the highest], it was 0.26, and in the case of the thick-film sample of 110 micrometers of thickness, even place [where the signal strength of Pb is the highest], it was 0.38.
[0034]
On the other hand, in the case of the thick thick-film sample of thickness, in the deep part near the front face of a substrate or a base, even if the signal strength of Pb is not only high, but it went to the thick-film front face, it became clear that the fall of the signal strength of Pb is also loose.
For example, in the case of the thick-film sample of 130 micrometers of thickness, the signal strength of Pb is right above [substrate], is 0.67 [highest] and is maintaining the signal strength of about 0.55 Pb to about 65 micrometers. In the case of the thick-film sample of 180 micrometers of thickness, the signal strength of Pb is 0.78 in the highest place, and is maintaining the signal strength of about 0.75 Pb to about 120 micrometers. In the case of the thick-film sample of 270 micrometers of thickness, the signal strength of Pb is 0.9 in the highest place, and is maintaining the signal strength of about 0.75 Pb to about 220 micrometers. In the case of the thick-film sample of 530 micrometers of thickness, the signal strength of Pb is 0.97 in the highest place, and is maintaining the signal strength of about 0.7 Pb to about

500 micrometers.

[0035]

In addition, although the signal strength of Cu was also measured in parallel to the signal strength of Pb in each above-mentioned thick-film sample, the signal strength of Cu showed almost fixed signal strength covering each location of each thick-film sample.

[0036]

It became clear that extent in which Pb is lost was stopped as extent in which Pb is lost at the time of baking was large and thickness became thick from the above thing so that the thickness of a thick-film sample was thin. That is, it is thought by suppressing volatilization of Pb from a thick-film sample front face as the thickness of a thick-film sample becomes thick, and suppressing the presentation gap resulting from Pb which has big effect on a superconduction property having been lost that Jc and Ic of a thick-film sample increased sharply.

[0037]

Furthermore, the 830-850-degree C baking conditions aiming at peeling suppression [front face / the substrate of a thick film or / of a base] were also effective at the beginning in the semantics of reducing the thermal activity of Pb in the viewpoint of controlling Pb being lost by vaporization. And when the effectiveness of reducing this thermal activity of Pb, and the effectiveness which thickens thickness act in multiplication, it is thought that it controlled that Pb was lost by vaporization and the presentation gap from a superconduction presentation is controlled from the thick film.

[0038]

Consequently, although Jc was able to obtain two or more 3800 A/cm and Ic was able to obtain the thick film more than 25A, these thick films can be applied to applications various as a practical oxides-superconductors thick film, and the oxide superconductivity structure by which this oxides-superconductors thick film is formed in the front face of a substrate or a base is considered [that it is applicable to the application of a current lead, magnetic shielding, etc., and].

[0039]

Hereafter, based on an example, this invention is further explained to a detail.

(Example)

Weighing capacity was carried out, it mixed and each powder of Bi 2O3, and PbO, SrCO3, CaCO3 and CuO was used as mixed powder so that it might become the mole ratio of 1.85:0.35:1.90:2.05:3.05.

Under the atmospheric-air ambient atmosphere, 780 degrees C, temporary quenching of this mixed powder was carried out for 10 hours, and it was used as temporary-quenching powder.

It put into the ceramic spot with both this temporary-quenching powder, the zirconia ball as grinding media, and the toluene as a solvent, and it set to the rotation base, ball grinding was performed, and the temporary-quenching powder of the shape of a slurry which ball grinding ended was dried with the dryer.

Again, under the atmospheric-air ambient atmosphere, 780 degrees C, after calcinating the temporary-quenching powder which this desiccation completed for 10 hours, ball grinding was carried out and it was dried. In addition, grinding conditions and desiccation conditions were performed on these 1st conditions.

And the line obtained superconduction composition powder for a series of actuation of this "baking-grinding-desiccation" 3 times.

[0040]

The superconduction paste was prepared by adding dibutyl phtalate as ethyl cellulose and an organic vehicle as an organic binder to the obtained superconduction composition powder, and kneading to it using 3 rollers.

After applying the prepared superconduction paste to the MgO polycrystal substrate with die length of 50mm, a width of face [of 5mm], and a thickness of 1mm by the thickness of 1060 micrometers and drying it, burning temperature of 835-840 degrees C and baking of 100 hours were performed.

Next, 3t /was pressurized by the pressure of 2 cm using CIP to the thick-film sample after baking, then burning temperature of 835-840 degrees C and baking of 100 hours were performed.

Consequently, the thick-film sample of 2+aSr2calcium2Cu3Oz which has 530-micrometer thickness (Bi, Pb) was obtained.
[0041]
The silver paste was used for the obtained thick-film sample, the electrode was prepared, it cooled to 77K by liquid nitrogen, and Ic was measured by 4 terminal method (electrization). Next, Jc was computed from the cross section of measured Ic and a sample.
Consequently, Ic of this thick-film sample showed 165A, and Jc showed 6226 A/cm2.
[0042]
(Example 1 of a comparison)
After applying the superconduction paste same with having prepared in the example to the MgO polycrystal substrate with die length of 50mm, a width of face [of 5mm], and a thickness of 1mm by the thickness of 180 micrometers like the example and drying it, burning temperature of 835-840 degrees C and baking of 100 hours were performed. Next, 3t /was pressurized by the pressure of 2 cm using CIP to the thick-film sample after baking, then burning temperature of 835-840 degrees C and baking of 100 hours were performed. Consequently, the thick-film sample of 2+aSr2calcium2Cu3Oz which has 90-micrometer thickness (Bi, Pb) was obtained. Jc of the obtained thick-film sample was 700 A/cm2, and Ic was 3.15A.
[0043]
Using the superconduction composition powder obtained on the other hand while preparing a superconduction paste, burning temperature of 835-840 degrees C and baking of 100 hours were performed, and 1.5mm in the diameter of 25mm and thickness which have the same raw material presentation as a superconduction paste, and the bulk object sample of consistency about 5.1 g/cm3** were prepared. Jc(s) of this bulk object sample were about 5000 A/cm3.
[0044]
Here, quantitative analysis by ICP was carried out about the concentration of each element which removes and extracts the prepared thick film of a thick-film sample, and is contained in a thick film, and quantitative analysis by ICP was carried out to coincidence also about the concentration of each element in a bulk object sample.
This analysis result is explained referring to drawing 6 . However, in the table of drawing 6 , the quantum result of the bulk object sample about each element of Bi, Pb, Sr, calcium, and Cu was standardized as 1, and the quantum result of each element in the thick-film sample to it is computed and indicated.
[0045]
From the result of drawing 6 , when the thick-film sample was compared with the bulk object sample, it became clear that Pb was conspicuous and was decreasing in a thick-film sample.
[0046]
Next, the line analysis trial of the direction of thickness was performed about Pb concentration in a thick-film sample by EPMA, and the result was shown in drawing 7 . In the graph of drawing 7 , an axis of ordinate shows the value of the signal strength of Pb in EPMA measurement. An axis of abscissa shows the scan location of an EPMA probe, the location of the interface of a substrate and a thick-film sample is about 43 micrometers, and the location on the front face of a thick film is about 136 micrometers.
[0047]
In the thick-film sample, Pb concentration was [right above / substrate] higher than the result of drawing 7 , and it became clear that it was decreasing toward a front face.
[0048]
In a baking process, on the surface of a thick film, Pb is lost by the 2(Bi, Pb)+aSr2calcium2Cu3Oz crystal from a near part, and the presentation gap from a superconduction presentation is mainly caused as a result from this drawing 6 and the result of 7 by the thick-film sample of the example of a comparison. And the presentation gap from this superconduction presentation is considered to be the cause that Jc of a thick-film sample falls compared with a bulk object.

[0049]
(Example 2 of a comparison)
Weighing capacity was carried out, it mixed and each powder of Bi 2O3, and SrCO3, CaCO3 and CuO was used as mixed powder so that it might become the mole ratio of 2:2:1:2.
Under the atmospheric-air ambient atmosphere, 800 degrees C, temporary quenching of this mixed powder was carried out, and it was used as temporary-quenching powder for 50 hours.
To this temporary-quenching powder, the line obtained the superconduction composition powder of Bi2Sr2calcium1Cu2Oy for a series of actuation of "baking-grinding-desiccation" 3 times like the example.
The superconduction paste of Bi2Sr2calcium1Cu2Oy was prepared by kneading the obtained superconduction composition powder like an example.
[0050]
After applying the prepared superconduction paste to six kinds of thickness, 65 micrometers, 130 micrometers, 170 micrometers, 210 micrometers, 260 micrometers, and 390 micrometers, and drying it to a MgO polycrystal substrate with die length of 50mm, a width of face [of 5mm], and a thickness of 1mm, liquation of the burning temperature of 890 degrees C and the baking for 10 minutes be performed and carried out, it cooled slowly over 10 hours to the burning temperature of 800 degrees C further, and the organization be crystallized
Consequently, the thick-film sample of six kinds of Bi2Sr2calcium1Cu2O(ies) which have thickness (50 micrometers, 100 micrometers, 130 micrometers, 160 micrometers, 200 micrometers, and 300 micrometers) was obtained.
[0051]
Jc and Ic of this thick-film sample were measured like the example.
The result is explained referring to drawing 4 , drawing 5 (a), and (b).
Drawing 4 is a table showing the measurement result of the thickness of six kinds of thick-film samples, and Jc and Ic. Drawing 5 (a) It is the graph by which took Jc (A/cm2) of a thick-film sample for the result of drawing 4 along the axis of ordinate, and the thickness (micrometer) of a thick-film sample was taken and shown on the axis of abscissa, and drawing 5 (b) is the graph by which took Ic (A) of a thick-film sample for the result of drawing 4 along the axis of ordinate, and the thickness (micrometer) of a thick-film sample was taken and shown on the axis of abscissa. In addition, the account of the average of the measurement result in the example of the thick-film sample which starts this invention in drawing 5 (a) and (b) was carried out with the dashed line for the comparison.
[0052]
When the thickness of the thick film formed in the MgO substrate was 50 micrometers so that more clearly than drawing 4 and drawing 5 (a), as for Jc of a thick-film sample, 6000 A/cm2 was shown, but the value of Jc decreased rapidly continuously with the increment in thickness, and when thickness was 300 micrometers, Jc of a thick-film sample became 2067 A/cm2.
[0053]
On the other hand, although the thickness of a thick film showed 15A in 50 micrometers, it was only increasing gradually with the increment in thickness, and Ic of a thick-film sample was 31A also in 300 micrometers of thickness, so that more clearly than drawing 4 and drawing 5 (b).
[0054]
[Effect of the Invention]
As explained in full detail above, the thick film characterized by being the oxides superconductors which contain Bi, Pb, Sr, calcium, and Cu to the front face of a substrate or a base, and thickness being 130 micrometers or more in order that this invention may obtain the thick film of the oxides superconductors which have high Jc and high Ic was able to be formed, and the thick film of the oxides superconductors which have Jc and Ic which arrive at a practical use field was able to be obtained.
[Brief Description of the Drawings]
[Drawing 1] It is the table having shown the measurement result of the thickness of the thick-film sample concerning this invention, Jc, and Ic.

[Drawing 2] It is the graph of the thickness of the thick-film sample concerning this invention, and Jc and Ic.
[Drawing 3] It is the graph which showed the line analysis measurement result of Pb concentration in the direction of thickness of the thick-film sample concerning this invention.
[Drawing 4] It is the table having shown the measurement result of the thickness of the thick-film sample concerning the example of a comparison, Jc, and Ic.
[Drawing 5] It is the graph of the thickness of the thick-film sample concerning the example of a comparison, and Jc and Ic.
[Drawing 6] It is the table having shown the analysis result of the configuration element of a bulk object sample and the thick-film sample concerning a Prior art.
[Drawing 7] It is the graph which showed the line analysis result of the direction of thickness of Pb in the thick-film sample concerning the example of a comparison.
[Drawing 8] It is the graph of the thickness of the thick-film sample concerning this invention, and the maintenance rate of Pb in a thick film.

[Translation done.]

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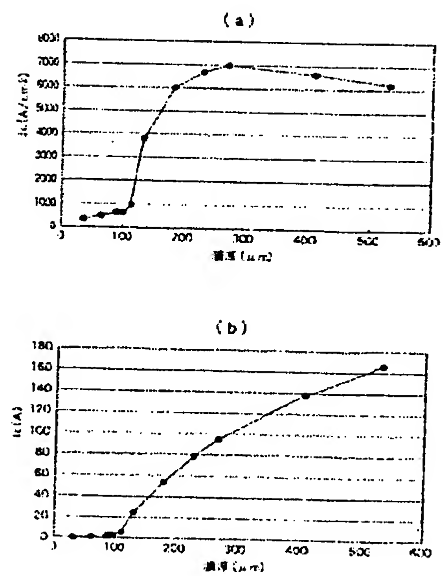
(54)【発明の名称】酸化物超電導体厚膜およびその製造方法

(57)【要約】
【課題】基板または基体の表面に形成され高いＪｃとＩｃとを有する酸化物超導体の厚膜と、その製造方法とを提供する。
【解決手段】Ｂｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕの各元素を含む原料の所定量を、秤量・混合し仮焼、粉砕、乾燥の工程の後、有機バインダーと有機ビヒクルとを加え $(Bi、Pb)_{2+a}Sr_2Ca_2Cu_3O_z$ 超電導ペーストを調製し、基板または基体の表面へ２６０μm以上の厚みに塗布し、乾燥した後に、まず温度８３５～８４０℃、１００時間の焼成をおこない、次に加圧をおこない、さらに温度８３５～８４０℃、１００時間の焼成をおこなうことで、高いＪｃとＩｃとを有する膜厚１３０μm以上の酸化物超電導体の厚膜を調製する。



【特許請求の範囲】
【請求項１】
基板または基体の表面に形成されるＢｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕを含む酸化物超電導体の厚膜であって、
前記厚膜の膜厚が１３０μｍ以上であることを特徴とする酸化物超電導体厚膜。
【請求項２】
基板または基体の表面へ酸化物超電導合成粉を塗布し、これを焼成して形成されるＢｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕを含む酸化物超電導体の厚膜であって、
前期塗布された酸化物超電導合成粉に含有されていたＰｂの３０ｗｔ％以上が、前記厚膜中に保持されていることを特徴とする酸化物超電導体厚膜。
【請求項３】
基板または基体の表面に形成されるＢｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕを含む酸化物超電導体の厚膜であって、
Ｂｉ：Ｐｂ：Ｓｒ：Ｃａ：Ｃｕ＝１．８５：０．３５：１．９０：２．０５：３．０５のモル比を有する酸化物超電導合成粉を８５０℃、１００時間焼成した後、ＣＩＰを用いて３トン／cm^2 の圧力で圧縮し、さらに８５０℃、１００時間焼成して $(Bi, Pb)_{2+a}Sr_2Ca_2Cu_3O_z$（但し、０＜ａ＜０．５）を含む酸化物超電導体のバルク体を調製し、ＥＰＭＡにより、そのバルク体中心部に含まれるＰｂの信号強度を測定し、その信号強度を１と規格化したとき、
ＥＰＭＡにより、前記基板または基体の表面直上の前記厚膜に含まれるＰｂの信号強度を測定した際の、Ｐｂの信号の相対強度が０．６７以上であることを特徴とする酸化物超電導体厚膜。
【請求項４】
基板または基体の表面に、請求項１から３のいずれかに記載の酸化物超電導体厚膜が形成されていることを特徴とする酸化物超電導構造体。
【請求項５】
基板または基体の表面に形成されるＢｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕを含む酸化物超電導体の厚膜の製造方法であって、
前記厚膜を作製する際、前記基板または基体の表面へ酸化物超電導体ペーストを２６０μｍ以上の膜厚になるよう塗布し、８３０～８５０℃の焼成温度で焼成することを特徴とする酸化物超電導体厚膜の製造方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】
本発明は、高い臨界電流密度を有するＢｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕを含む酸化物超電導体の厚膜、およびその製造方法に関する。
【０００２】
【従来の技術】
ＭｇＯ、アルミナ、ＹＳＺなどの酸化物基板または酸化物基体、並びにＡｇ、Ａｕ、Ｐｔ、Ｎｉなどの金属基板または金属基体に、酸化物超電導体を膜状に形成して機能させることにより様々な応用製品が考案されている。
この酸化物超電導体を膜状に形成する方法として、酸化物超電導体粉末である酸化物超電導合成粉に適当な有機バインダーを添加してペースト状にした後、スクリーン印刷法、ドクターブレード法、スプレー法等を用いて前記基板または基体の表面に塗布し焼成して、多結晶体の酸化物超電導体の厚膜を形成させる手法が試みられている。
【０００３】
この酸化物超電導体の厚膜を形成させる手法は、高価な単結晶基板や、ＰＶＤ、ＣＶＤなどに代表される高真空系を必要とする大掛かり、かつ高価な装置を必要としないことより、製造コストの面で非常に安価、有利であり、実用化に最も近い手法であると考えられている。
従来、この厚膜を形成させる酸化物超電導体材料としては、$Y_1Ba_2Cu_3O_x$ の組成を有するＹＢＣＯ系、$Bi_2Sr_2Ca_1Cu_2O_y$ の組成を有するＢｉ２２１２系、$(Bi, Pb)_{2+a}Sr_2Ca_2Cu_3O_z$（但し、０＜ａ＜０．５が一般的である、以下同じ。）の組成を有するＢｉ２２２３系が主に試みられてきた。
ここで酸化物超電導体の厚膜を実用的な製品に応用する場合、液体窒素温度において臨界電流密度（以下、Ｊｃと記載する。）は、３，５００Ａ／cm^2 以上、が求められる。
この観点から、上述した酸化物超電導体の従来の技術について簡単に説明する。
【０００４】
例えば、$Y_1Ba_2Cu_3O_x$ を含む酸化物超電導体厚膜（以下、厚膜と記載する。）は、液体窒素温度においてＪｃとして数百Ａ／cm^2 が得られている。臨界電流値（以下、Ｉｃと記載する。）については、幅５ｍｍ、厚さ１００μｍの厚膜試料により数Ａ程度が得られている。
しかし、$Y_1Ba_2Cu_3O_x$ は、酸化物超電導体の厚膜すなわち多結晶体の形態をとった場合、結晶方位が揃い難いため、上記以上のＪｃを得ることが困難である。
【０００５】
また、例えば、$Bi_2Sr_2Ca_1Cu_2O_y$ を含む厚膜は、液体窒素温度においてＪｃとして６０００Ａ／cm^2 が得られ、Ｉｃについては、幅５ｍｍ、厚さ５０μｍの厚膜試料により約１０～１５Ａが得られている等、有望な材料である。
しかしこの材料は、より高いＩｃを得るために試料膜厚を厚くしていくと、超電導特性が急激に低下してしまう。その結果、膜厚を厚くすればするほど、厚膜全体として平均化したＪｃの値は低下していき、例えば、幅５ｍｍ、厚さ１００μｍの厚膜を作製してもＩｃは２０Ａ程度であり、Ｊｃでは約４０００Ａ／cm^2 まで低下し

てしまう。そして、これ以上、膜厚を厚くしてもＩｃはそれに比例して大きくはならず、逆に平均化したＪｃは低下の一途を辿ってしまう。

【０００６】

また、例えば、（Ｂｉ、Ｐｂ）$_{2+a}$Ｓｒ$_2$Ｃａ$_2$Ｃｕ$_3$Ｏ$_z$を含む厚膜は、現在迄のところ厚さ１００μｍの厚膜試料が製造され、液体窒素温度においてＪｃとして数百Ａ／ｃｍ^2、Ｉｃとして、幅５ｍｍの試料により数Ａ程度が得られている。ところが、この厚膜の示すＪｃは、同様の（Ｂｉ、Ｐｂ）$_{2+a}$Ｓｒ$_2$Ｃａ$_2$Ｃｕ$_3$Ｏ$_z$を含むバルク体が有するＪｃの値から期待される値の１／１０程度である。さらに、より高いＩｃを得るために厚膜の膜厚を１００μｍ以上に厚くしていくと、前記焼成の際に、酸化物超電導体が基板または基体の表面より剥がれてしまうため、（Ｂｉ、Ｐｂ）$_{2+a}$Ｓｒ$_2$Ｃａ$_2$Ｃｕ$_3$Ｏ$_z$を含む酸化物超電導体は、厚膜用材料として困難視されている。

【０００７】

【発明が解決しようとする課題】

上述の状況より、本発明が解決しようとする課題は、高いＪｃおよびＩｃを有する酸化物超電導体の厚膜と、その製造方法とを提供することである。

【０００８】

【課題を解決するための手段】

本発明に係る、課題を解決するための第１の手段は、基板または基体の表面に形成されるＢｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕを含む酸化物超電導体の厚膜であって、

前記厚膜の膜厚が１３０μｍ以上であることを特徴とする酸化物超電導体厚膜である。

【０００９】

基板または基体の表面に形成されるＢｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕを含む酸化物超電導体の厚膜の膜厚を１３０μｍ以上とすることで、厚膜の有するＪｃおよびＩｃを大きく向上させることができた。

【００１０】

第２の手段は、基板または基体の表面へ酸化物超電導合成粉を塗布し、これを焼成して形成されるＢｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕを含む酸化物超電導体の厚膜であって、

前期塗布された酸化物超電導合成粉に含有されていたＰｂの３０ｗｔ％以上が、前記厚膜中に保持されていることを特徴とする酸化物超電導体厚膜である。

【００１１】

上記の構成を有し、基板または基体の表面に形成されるＢｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕを含む酸化物超電導体の厚膜は、高いＪｃおよびＩｃを有していた。

【００１２】

第３の手段は、基板または基体の表面に形成されるＢｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕを含む酸化物超電導体の厚膜であって、

Ｂｉ：Ｐｂ：Ｓｒ：Ｃａ：Ｃｕ＝１．８５：０．３５：１．９０：２．０５：３．０５のモル比を有する酸化物超電導合成粉を８５０℃、１００時間焼成した後、ＣＩＰを用いて３トン／ｃｍ^{2}の圧力で圧縮し、さらに８５０℃、１００時間焼成して（Ｂｉ、Ｐｂ）$_{2+a}$Ｓｒ$_2$Ｃａ$_2$Ｃｕ$_3$Ｏ$_z$（但し、０＜ａ＜０．５）を含む酸化物超電導体のバルク体を調製し、ＥＰＭＡにより、そのバルク体中心部に含まれるＰｂの信号強度を測定し、その信号強度を１と規格化したとき、

ＥＰＭＡにより、前記基板または基体の表面直上の前記厚膜に含まれるＰｂの信号強度を測定した際の、Ｐｂの信号の相対強度が０．６７以上であることを特徴とする酸化物超電導体厚膜である。

【００１３】

上記の構成を有し、基板または基体の表面に形成されるＢｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕを含む酸化物超電導体の厚膜は、高いＪｃおよびＩｃを有していた。

【００１４】

第４の手段は、基板または基体の表面に、第１から第３の手段のいずれかに記載の酸化物超電導体厚膜が形成されていることを特徴とする酸化物超電導構造体である。

【００１５】

上記の構成により、高いＪｃおよびＩｃを有する酸化物超電導構造体を、安価な製造コストで得ることができた。

【００１６】

第５の手段は、基板または基体の表面に形成されるＢｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕを含む酸化物超電導体の厚膜の製造方法であって、

前記厚膜を作製する際、前記基板または基体の表面へ酸化物超電導体ペーストを２６０μｍ以上の膜厚になるよう塗布し、８３０～８５０℃の焼成温度で焼成することを特徴とする酸化物超電導体厚膜の製造方法である。

【００１７】

上記の製造方法を採ることにより、１３０ｍμ以上の膜厚を有するＢｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕを含む酸化物超電導体の厚膜を製造することができる。

【００１８】

【発明の実施の形態】

本発明者は、高いＪｃ、Ｉｃを有する酸化物超電導体の厚膜を得るために、Ｂｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕを含む酸化物超電導合成粉を調製し、有機バインダーおよび溶媒を添加してペースト状にした後、基板または基体の表面に塗布して、塗布されたペーストの焼成温度と、基板または基体の表面よりの剥がれとの関係について検討をおこなった。その結果、従来行われている８５０℃を超える温度で焼成を実施すると、（Ｂｉ、Ｐｂ）$_{2+a}$Ｓｒ$_2$Ｃａ$_2$Ｃｕ$_3$Ｏ$_z$の結晶成長速度が大きいため、厚膜の、基板および基板表面方向への成長が急激に進行し、この結果、基板または基体の表面よりの剥がれが引

き起こされることを解明した。

【0019】

そこで本発明者は、上述の剥がれを抑制するために試行錯誤を重ねた結果、$(Bi、Pb)_{2-a}Sr_2Ca_2Cu_3O_z$厚膜を、従来の焼成温度より低い温度である830～850℃、より好ましくは835～840℃の範囲で焼成することにより、130μm以上の厚膜を基板または基体の表面に成膜しても剥がれが起きないばかりか、厚膜のJcおよびIcが大きく増加することを見出した。

【0020】

以下、Bi、Pb、Sr、Ca、Cuを含む酸化物超電導体の厚膜の例として、基板または基体の表面に塗布されたBi、Pb、Sr、Ca、Cuを含む酸化物超電導合成粉のペースト（以下、超電導ペーストと記載する。）を焼成して得られた厚膜を例として説明する。

【0021】

Bi_2O_3、PbO、$SrCO_3$、$CaCO_3$、CuOの各種粉末を、所望のモル比となるように秤量し混合する。このとき$CaCO_3$はCaOまたは$Ca(OH)_2$でもよい。また、湿式共沈法等にてBi、Pb、Sr、Ca、Cuの各元素を所望のモル比になるよう調製した原料を使用してもよい。

次に、この混合粉を仮焼し仮焼粉を得る。仮焼条件は600℃～1000℃より好ましくは750℃～850℃で、3時間～50時間である。

次に上記仮焼粉を、ジルコニアボールおよびトルエン等の有機溶媒とともにセラミックスポットに入れてボール粉砕をおこなう。この操作によって、仮焼粉を細かく粉砕して均一性を向上させるとともに、次の焼成工程において仮焼粉の熱的反応性を上げることができる。

【0022】

ボール粉砕が終了したスラリー状の仮焼粉を乾燥機で乾燥させる。

次に、乾燥後の仮焼粉を750～850℃、3～50時間の焼成条件で焼成後、上述したボール粉砕を行い、以降、この「焼成－ボール粉砕－乾燥」を1～5回（好ましくは2～3回）繰り返し超電導合成粉を調製した。

調製された超電導合成粉を適宜な有機バインダーおよび有機ビヒクルと混合し、3本ローラー等を用いて混練することにより超電導ペーストを得た。

【0023】

得られた超電導ペーストを、基板または基体の表面に各種の膜厚で塗布、乾燥させた後に焼成して、酸化物超電導体の厚膜試料とした。

厚膜試料の膜厚は、概ね、塗布された超電導ペーストの膜厚の1／2となるので、例えば130μmの膜厚を得るには260μm程度、530μmの膜厚を得るには1060μm程度の厚みで超電導ペーストを塗布すればよい。

焼成条件は、焼成温度830～850℃：より好ましくは835～840℃で、焼成時間は50～100時間とした。

焼成後の厚膜試料へ、CIP（冷間静水圧プレス）装置を用いて2～3トン／cm^2の圧力で圧縮を行った。これは焼成により生成した$(Bi、Pb)_{2-a}Sr_2Ca_2Cu_3O_z$の板状結晶を、超電導電流が流れやすいab面を通電方向にそろえるように配向させるためである。

加圧・圧縮後の厚膜試料を、再度、焼成温度830～850℃、より好ましくは835～840℃、焼成時間は50～100時間で焼成した。

【0024】

すると100μm以上の膜厚を有する厚膜試料であっても、焼成後に基板または基体の表面より剥がれを起こすことがなく、膜厚1000μm程度を有する厚膜試料まで調製することが可能となった。

この結果、本実施の形態においては膜厚30～530μmを有する11種類の$(Bi、Pb)_{2+a}Sr_2Ca_2Cu_3O_z$厚膜試料を調製した。

【0025】

この11種類の厚膜試料が示した超電導特性のJc、Icについて、図1、図2（a）（b）を参照しながら説明する。

図1は、11種類の厚膜試料の膜厚とJc、Icとの測定結果とを表した表であり、図2（a）は、図1の結果を縦軸に厚膜試料のJc（A／cm^2）をとり、横軸に厚膜試料の焼成後の膜厚（μm）をとって示したグラフであり、図2（b）は、図1の結果を縦軸に厚膜試料のIc（A）をとり、横軸に厚膜試料の膜厚（μm）をとって示したグラフである。

尚、厚膜試料のJc、Ic測定は、厚膜試料に銀ペーストを用いて電極を設け、液体窒素により77Kに冷却して、4端子法（通電法）にてIcを測定し、次に測定されたIcと試料の断面積よりJcを算出しておこなった。

【0026】

図1および図2（a）より明らかなように、基板または基体の表面に形成された厚膜の膜厚が110μm以下の場合、厚膜試料のJcは膜厚の増加とともに漸増するがその値は、30μmで400A／cm^2程度、110μmで1000A／cm^2程度である。ところがこれより膜厚が厚くなるとJcの値は大幅に増加し、130μmで3850A／cm^2程度、270μmで7000A／cm^2程度に達する。

膜厚がこれ以上厚くなってもJcの増加はみられず、むしろ漸減傾向がみられたが、膜厚530μmにおいても6200A／cm^2を示した。

【0027】

一方、図1および図2（b）より明らかなように、厚膜

試料のＩｃは、厚膜の膜厚が１１０μｍ以下の場合、膜厚の増加とともに漸増し、３０μｍで０．６Ａ程度、１１０μｍで５．５Ａ程度である。ところがこれより膜厚が厚くなるとＩｃの値は大幅に増加し、１３０μｍで２５Ａ程度、２７０μｍで９５Ａ程度に達し、さらに膜厚の増加とともに増加を続け、５３０μｍで１６５Ａ程度に達した。

【００２８】

次に、調製した１１種類の厚膜試料より、膜厚８５μｍ、１１０μｍ、１３０μｍ、１８０μｍ、２７０μｍおよび５３０μｍの６種類の厚膜試料を選択し、その厚膜を剥がして採取し厚膜中に含まれるＰｂ濃度についてＩＣＰによる定量分析を行い、同時に、超電導ペーストとして用いた超電導合成粉のＰｂ濃度についてもＩＣＰによる定量分析を行った。

この結果について、図８を参照しながら説明する。

図８は、縦軸に、超電導ペーストとして用いた超電導合成粉のＰｂ濃度と厚膜試料に含まれるＰｂ濃度とから算出した、超電導合成粉から厚膜試料中へのＰｂの保持割合をとり、横軸に、厚膜試料の膜厚値をとったグラフである。

【００２９】

図８より、厚膜試料の膜厚値が１１０μｍ以下の場合は、Ｐｂの保持割合が２０％未満であることが判明した。これに対し、膜厚値が１３０μｍの場合は、Ｐｂの保持割合が３０％を超え、その後、膜厚値の増加とともにＰｂの保持割合も増加していくことが判明した。

【００３０】

更に、膜厚８５μｍ、１１０μｍ、１３０μｍ、１８０μｍ、２７０μｍおよび５３０μｍの６種類の厚膜試料に対し、ＥＰＭＡを用いて、厚膜中に含まれるＰｂ濃度について膜厚方向の線分析を行った。

この結果について、図３を参照しながら説明する。

図３は、縦軸に、厚膜試料の膜厚方向に含まれるＰｂの信号の相対強度をとり、横軸に、厚膜試料における膜厚方向の位置を示したグラフである。

ここで、前記Ｐｂの信号の相対強度は、以下の方法により求めた。

【００３１】

まず、Bi_2O_3、ＰｂＯ、$SrCO_3$、$CaCO_3$、ＣｕＯの各粉末を、１．８５：０．３５：１．９０：２．０５：３．０５のモル比となるように秤量し混合して混合粉とした。

この混合粉を、大気雰囲気下で７８０℃、１０時間仮焼して仮焼粉とした。

この仮焼粉と、粉砕メディアとしてのジルコニアボール、溶媒としてのトルエンと共にともにセラミックスポットに入れて、回転台にセットしボール粉砕をおこない、ボール粉砕が終了したスラリー状の仮焼粉を乾燥機で乾燥させた。

この乾燥が完了した仮焼粉を、再度、大気雰囲気下で７８０℃、１０時間焼成した後、ボール粉砕し、乾燥させた。尚、粉砕条件、乾燥条件は１回目と同条件で行った。

そしてこの「焼成－粉砕－乾燥」の一連の操作を３回行って、超電導合成粉を得た。

【００３２】

上記の工程で得られた超電導合成粉を、８５０℃、１００時間焼成した後、ＣＩＰを用いて３トン／ｃｍ^{2}の圧力で圧縮し、さらに８５０℃、１００時間焼成して$(Bi,Pb)_{2+a}Sr_2Ca_2Cu_3O_z$の組成を有する直径２５ｍｍ、厚さ１．５ｍｍの酸化物超電導体のバルク体を調製した。このバルク体の一例は、密度約５．１ｇ／ｃｍ^3、Ｊｃ約５０００Ａ／ｃｍ^{2}を示した。

前記バルク体中心部に含まれるＰｂの信号強度をＥＰＭＡにより測定し、その信号強度を１と規格化する。

一方、厚膜試料において基板または基体の表面直上の位置を０μｍとし、そこから厚膜表面への距離をもって厚膜中の位置を示し、その各位置に含まれるＰｂの信号強度をＥＰＭＡにより測定し、規格化した前記バルク体の信号強度との相対強度を算出して求めた。

尚、前記バルク体と前記厚膜試料とのＥＰＭＡ測定における測定条件を一致させるため、両試料は同時に測定することが好ましい。

さらに、図３において、前記厚膜試料のうち、膜厚８５μｍの試料は実線で、１１０μｍの試料は破線で、１３０μｍの試料は太実線で、１８０μｍの試料は太一点鎖線で、２７０μｍの試料は太二点鎖線で、５３０μｍの試料は太破線で示した。

【００３３】

図３の結果より明らかなように、膜厚の薄い厚膜試料の場合、厚膜の表面のみならず、最も基板または基体の表面に近い深部においても、Ｐｂの信号強度が低下していることが判明した。

例えば、膜厚８５μｍの厚膜試料の場合、Ｐｂの信号強度は最も高いところでも０．２６であり、膜厚１１０μｍの厚膜試料の場合、Ｐｂの信号強度は最も高いところでも０．３８であった。

【００３４】

これに対し、膜厚の厚い厚膜試料の場合、基板または基体の表面に近い深部において、Ｐｂの信号強度が高いのみならず、厚膜表面へ向かってもＰｂの信号強度の低下が緩やかなことも判明した。

例えば、膜厚１３０μｍの厚膜試料の場合、Ｐｂの信号強度は基板直上で、最も高い０．６７であり、６５μｍ程度まで０．５５程度のＰｂの信号強度を維持している。膜厚１８０μｍの厚膜試料の場合、Ｐｂの信号強度は最も高いところで０．７８であり、１２０μｍ程度まで０．７５程度のＰｂの信号強度を維持している。膜厚２７０μｍの厚膜試料の場合、Ｐｂの信号強度は最も高

いところで０．９であり、２２０μm程度まで０．７５程度のＰｂの信号強度を維持している。膜厚５３０μmの厚膜試料の場合、Ｐｂの信号強度は最も高いところで０．９７であり、５００μm程度まで０．７程度のＰｂの信号強度を維持している。

【００３５】

尚、上記の各厚膜試料においてＰｂの信号強度と並行してＣｕの信号強度も測定したが、Ｃｕの信号強度は各厚膜試料の各位置にわたって、ほぼ一定の信号強度を示した。

【００３６】

以上のことより、厚膜試料の膜厚が薄いほど、焼成時にＰｂが失われる程度が大きく、膜厚が厚くなるに従って、Ｐｂが失われる程度が抑えられていることが判明した。すなわち厚膜試料の膜厚が厚くなるに従って厚膜試料表面からのＰｂの揮発が抑えられ、超電導特性に大きな影響を及ぼすＰｂが失われたことに起因する組成ずれが抑えられることにより、厚膜試料のＪｃおよびＩｃが大幅に増加したものと考えられる。

【００３７】

さらに、当初は、厚膜の基板または基体の表面よりの剥がれ抑止を目的としていた８３０～８５０℃の焼成条件も、Ｐｂが揮散により失われるのを抑制するという観点においてＰｂの熱的活性を低下させるという意味で効果的であった。そして、このＰｂの熱的活性を低下させる効果と、膜厚を厚くする効果とが相乗的に作用することにより、厚膜よりＰｂが揮散により失われるのを抑制し、超電導組成からの組成ずれを抑制していると考えられる。

【００３８】

この結果、Ｊｃが３８００Ａ／ｃｍ^{2}以上、Ｉｃが２５Ａ以上の厚膜を得ることができたが、これらの厚膜は実用的な酸化物超電導体厚膜として多様な用途に適用可能であり、基板または基体の表面に、この酸化物超電導体厚膜が形成されている酸化物超電導構造体は、例えば電流リード、磁気シールド等の用途に適用可能であると考えられる。

【００３９】

以下、実施例に基づいて本発明をさらに詳細に説明する。

（実施例）

Bi_2O_3、ＰｂＯ、$SrCO_3$、$CaCO_3$、ＣｕＯの各粉末を、１．８５：０．３５：１．９０：２．０５：３．０５のモル比となるように秤量し混合して混合粉とした。

この混合粉を、大気雰囲気下で７８０℃、１０時間仮焼して仮焼粉とした。

この仮焼粉と、粉砕メディアとしてのジルコニアボール、溶媒としてのトルエンと共にともにセラミックスポットに入れて、回転台にセットしボール粉砕をおこない、ボール粉砕が終了したスラリー状の仮焼粉を乾燥機で乾燥させた。

この乾燥が完了した仮焼粉を、再度、大気雰囲気下で７８０℃、１０時間焼成した後、ボール粉砕し、乾燥させた。尚、粉砕条件、乾燥条件は１回目と同条件で行った。

そしてこの「焼成－粉砕－乾燥」の一連の操作を３回行って、超電導合成粉を得た。

【００４０】

得られた超電導合成粉へ、有機バインダーとしてエチルセルロース、有機ビヒクルとしてフタル酸ジブチルを加え３本ローラーを用いて混練することにより超電導ペーストを調製した。

調製した超電導ペーストを、長さ５０mm、幅５mm、厚さ１mmのＭｇＯ多結晶基板へ１０６０μmの厚みで塗布し、乾燥させた後、焼成温度８３５～８４０℃、１００時間の焼成をおこなった。

次に、焼成後の厚膜試料へＣＩＰを用いて、３トン／ｃｍ^{2}の圧力で加圧を行い、続いて、焼成温度８３５～８４０℃、１００時間の焼成をおこなった。

この結果、５３０μmの膜厚を有する$(Bi,Pb)_{2+a}Sr_2Ca_2Cu_3O_z$の厚膜試料が得られた。

【００４１】

得られた厚膜試料に銀ペーストを用いて電極を設け、液体窒素により７７Ｋに冷却して、４端子法（通電法）にてＩｃを測定した。次に測定されたＩｃと試料の断面積よりＪｃを算出した。

その結果、この厚膜試料のＩｃは１６５Ａ、Ｊｃは６２２６Ａ／ｃｍ^{2}を示した。

【００４２】

（比較例１）

実施例で調製したのと同様の超電導ペーストを、実施例と同様に、長さ５０mm、幅５mm、厚さ１mmのＭｇＯ多結晶基板へ１８０μmの厚みで塗布し、乾燥させた後、焼成温度８３５～８４０℃、１００時間の焼成をおこなった。次に、焼成後の厚膜試料へＣＩＰを用いて３トン／ｃｍ^{2}の圧力で加圧を行い、続いて、焼成温度８３５～８４０℃、１００時間の焼成をおこなった。この結果、９０μmの膜厚を有する$(Bi,Pb)_{2+a}Sr_2Ca_2Cu_3O_z$の厚膜試料が得られた。得られた厚膜試料のＪｃは７００Ａ／ｃｍ^2、Ｉｃは３．１５Ａであった。

【００４３】

一方、超電導ペーストを調製する途中で得られる超電導合成粉を用い、焼成温度８３５～８４０℃、１００時間の焼成をおこなって、超電導ペーストと同じ原料組成を有する、直径２５mm、厚さ１．５mm、密度約５．１ｇ／ｃｍ^3、のバルク体試料を調製した。このバルク体試料のＪｃは、約５０００Ａ／ｃｍ^{3}であった。

【００４４】

ここで、調製された厚膜試料の厚膜を剥がして採取し厚膜中に含まれる各元素の濃度についてＩＣＰによる定量分析を行い、同時に、バルク体試料中の各元素の濃度についてもＩＣＰによる定量分析を行った。
この分析結果について、図６を参照しながら説明する。但し、図６の表において、Ｂｉ、Ｐｂ、Ｓｒ、ＣａおよびＣｕの各元素についてのバルク体試料の定量結果を１として規格化し、それに対する厚膜試料中の各元素の定量結果を算出して記載している。

【００４５】
図６の結果より、厚膜試料とバルク体試料とを比較すると、厚膜試料においてはＰｂが際立って減少していることが判明した。

【００４６】
次に、ＥＰＭＡにより厚膜試料中のＰｂ濃度について膜厚方向の線分析試験を行い、その結果を図７に示した。図７のグラフにおいて、縦軸は、ＥＰＭＡ測定におけるＰｂの信号強度の値を示す。横軸は、ＥＰＭＡプローブの走査位置を示し、基板と厚膜試料との界面の位置は約４３μｍであり、厚膜表面の位置は約１３６μｍである。

【００４７】
図７の結果より、厚膜試料においてＰｂ濃度は基板直上で高く、表面へ向かって減少していることが判明した。

【００４８】
この図６、７の結果より、比較例の厚膜試料では焼成工程において、主に厚膜の表面に近い部分より $(Bi,Pb)_{2+a}Sr_2Ca_2Cu_3O_z$ 結晶よりＰｂが失われ、結果として超電導組成からの組成ずれを起こす。そしてこの超電導組成からの組成ずれが、バルク体に較べ厚膜試料のＪｃが低下する原因であると考えられる。

【００４９】
（比較例２）
Bi_2O_3、$SrCO_3$、$CaCO_3$、ＣｕＯの各粉末を、２：２：１：２のモル比となるように秤量し混合して混合粉とした。
この混合粉を、大気雰囲気下で８００℃、５０時間、仮焼して仮焼粉とした。
この仮焼粉へ、実施例と同様にして「焼成－粉砕－乾燥」の一連の操作を３回行って、$Bi_2Sr_2Ca_1Cu_2O_y$ の超電導合成粉を得た。
得られた超電導合成粉を、実施例と同様に混練することにより $Bi_2Sr_2Ca_1Cu_2O_y$ の超電導ペーストを調製した。

【００５０】
調製した超電導ペーストを、長さ５０mm、幅５mm、厚さ１mmのＭｇＯ多結晶基板へ６５μｍ、１３０μｍ、１７０μｍ、２１０μｍ、２６０μｍおよび３９０μｍの６種類の厚みに塗布し、乾燥させた後、焼成温度８９０℃、１０分間の焼成をおこなって部分溶融させ、さらに焼成温度８００℃まで１０時間かけて徐冷を行い組織の結晶化を行った。
この結果、５０μｍ、１００μｍ、１３０μｍ、１６０μｍ、２００μｍおよび３００μｍの膜厚を有する６種類の $Bi_2Sr_2Ca_1Cu_2O_y$ の厚膜試料が得られた。

【００５１】
この厚膜試料のＪｃおよびＩｃを実施例と同様に測定した。
その結果について、図４、図５（ａ）（ｂ）を参照しながら説明する。
図４は、６種類の厚膜試料の膜厚とＪｃ、Ｉｃとの測定結果とを表した表であり、図５（ａ）は、図４の結果を縦軸に厚膜試料のＪｃ（A/cm^2）をとり、横軸に厚膜試料の膜厚（μｍ）をとって示したグラフであり、図５（ｂ）は、図４の結果を縦軸に厚膜試料のＩｃ（Ａ）をとり、横軸に厚膜試料の膜厚（μｍ）をとって示したグラフである。尚、比較のため、図５（ａ）（ｂ）において本発明に係る厚膜試料の実施例における測定結果を１点鎖線で並記した。

【００５２】
図４および図５（ａ）より明らかなように、ＭｇＯ基板に形成された厚膜の膜厚が５０μｍの場合、厚膜試料のＪｃは６０００A/cm^2 を示したが、膜厚の増加とともにＪｃの値は急減し続け、膜厚が３００μｍの場合、厚膜試料のＪｃは２０６７A/cm^2 となった。

【００５３】
一方、図４および図５（ｂ）より明らかなように、厚膜試料のＩｃは、厚膜の膜厚が５０μｍにおいて１５Ａを示したが、膜厚の増加とともに漸増するのみで、膜厚３００μｍにおいても３１Ａであった。

【００５４】
【発明の効果】
以上詳述したように本発明は、高いＪｃとＩｃとを有する酸化物超電導体の厚膜を得るために、基板または基体の表面へＢｉ、Ｐｂ、Ｓｒ、Ｃａ、Ｃｕを含む酸化物超電導体であって、膜厚が１３０μｍ以上であることを特徴とする厚膜を形成し、実用領域に到達するＪｃとＩｃとを有する酸化物超電導体の厚膜を得ることができた。

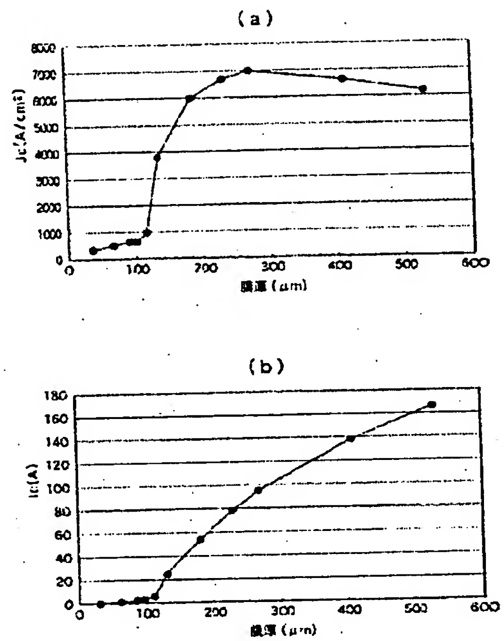
【図面の簡単な説明】
【図１】本発明に係る厚膜試料の膜厚とＪｃ、Ｉｃの測定結果を示した表である。
【図２】本発明に係る厚膜試料の膜厚とＪｃ、Ｉｃとのグラフである。
【図３】本発明に係る厚膜試料の膜厚方向におけるＰｂ濃度の線分析測定結果を示したグラフである。
【図４】比較例に係る厚膜試料の膜厚とＪｃ、Ｉｃの測定結果を示した表である。
【図５】比較例に係る厚膜試料の膜厚とＪｃ、Ｉｃとのグラフである。

【図６】バルク体試料と、従来の技術に係る厚膜試料との構成元素の分析結果を示した表である。
【図７】比較例に係る厚膜試料におけるＰｂの膜厚方向の線分析結果を示したグラフである。
【図８】本発明に係る厚膜試料の膜厚と、厚膜中のＰｂの保持割合とのグラフである。

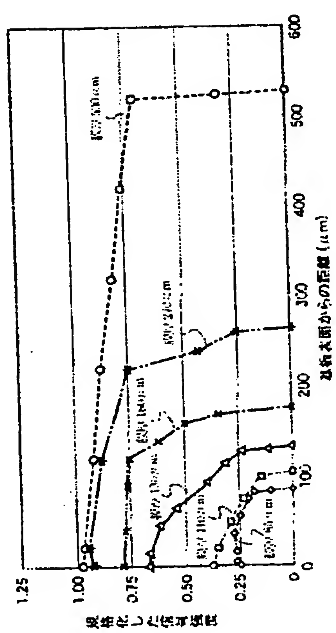
【図１】

膜厚(μm)	Jc (A/cm²)	Ic (A)
30	400	0.6
60	533	1.6
85	682	2.3
95	674	3.2
110	1000	5.5
130	3846	25
160	6000	54
230	6783	78
270	7037	95
410	6683	137
530	6226	165

【図２】



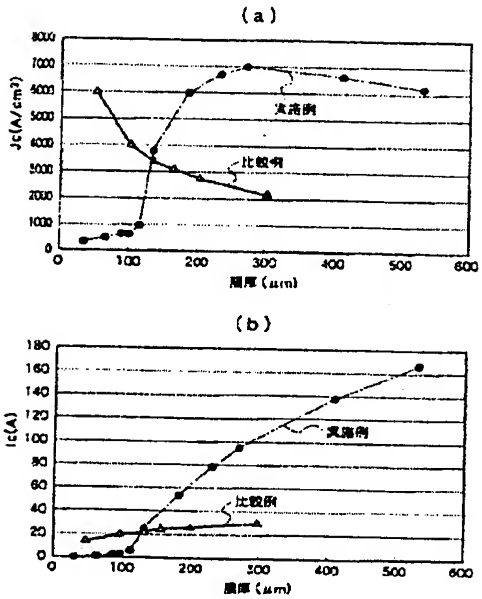
【図３】



【図４】

膜厚(μm)	Jc (A/cm²)	Ic (A)
50	6000	15
100	4000	20
130	3385	22
160	3125	25
200	2700	27
300	2067	31

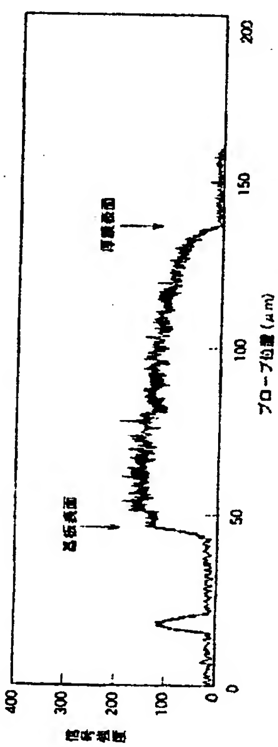
【図５】



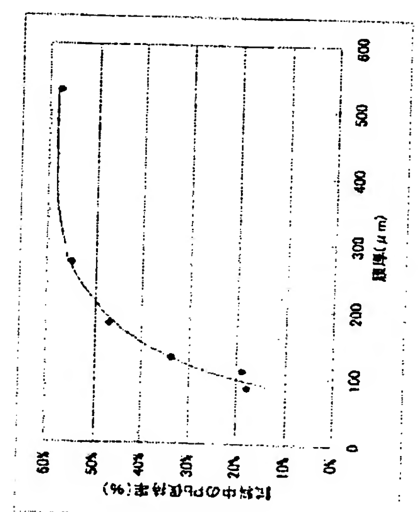
【図６】

	Bi	Pb	Sr	Ca	Cu
バルク体試料	1	1	1	1	1
厚膜試料	0.97	0.13	1.04	1.01	1.00

【図７】



【図８】



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